LONG-TERM AIR - SOIL EXCHANGES OF PCBs

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Abstract

Archived soils collected from five different long-term agricultural experiments in southern England have been analysed retrospectively for a range of PCB congeners. The change in soil PCB concentration over time has been similar in each field experiment, namely that soil samples exhibited a sharp rise in soil PCB concentrations between about 1940 and the early 1960s, reaching a maximum (ca. 140 - 560 μg ΣPCB/kg soil) during the late 1960s / early 1970s. Since then there has been a dramatic reduction in ΣPCB concentrations, such that contemporary concentrations (ca. 20-30 μg/kg) are now similar to those of the early 1940s soils. If these soil loadings were reflected nationwide, the ΣPCB burden of UK soils has fallen from *ca.* 26,600 t in 1970 to a contemporary burden of *ca.* 1,500 t. Volatilisation and subsequent long range transport probably account for the bulk of this loss. A total of 67,000 t of PCBs were manufactured in the UK between 1954 and 1977, with an estimated 40,000 t used within the UK. There has been a gradual shift in the relative proportion of individual congeners since the peak, with a move towards greater proportions of the heavier homologue groups in the most recent samples.

Introduction

Atmospheric deposition is the major source of PCBs to the terrestrial environment and has resulted in trace levels of PCBs being present in all soils. Their commercial production started in the USA in 1929, with world production reaching a maximum in the early 1960s. Because of elevated levels found in a range of environmental samples, their industrial use in much of Europe and America has been restricted since the mid 1970s. Despite these legislative controls, contemporary PCB concentrations in marine predators are still high enough to be linked to adverse ecotoxicological effects. The objective of this study was to establish the long-term temporal trends of PCBs in UK soils and to

set this in context with contemporary PCB concentrations in UK soils. This has been achieved by analysis of a set of archived soil samples from long term agricultural plots established at Rothamsted Experimental Station.

Materials and Methods

Samples of surface (0-23 or 0-15 cm) soils from 5 different long-term agricultural experiments have been analysed. Soils from the various sites have been collected, processed and stored in the same way over many decades. A full account of the samples, their collection, extraction and analysis procedures are given in ref. 1. The following congeners were routinely detected and quantified in all the samples: 6, 8, 14, 18, 28, 52, 104, 44, 40, 61, 66, 101, 99, 110, 151, 149, 118, 188, 153, 105, 138, 183, 180, 170, 201 and 194/205.

Results

Figure 1 shows the temporal trend of ΣPCB concentrations found in the archived soil samples between 1944 and 1992. The pattern is similar in each soil series analysed, namely that soil samples exhibit a sharp rise in soil PCB concentrations between about 1940 and the early 1960s, reaching a maximum during the late 1960s / early 1970s. Since then there has been a dramatic reduction in ΣPCB concentrations at these sites, so that contemporary concentrations are now close to those of the early 1940s soils. The ΣPCB burden of each soil sample was dominated by the tri and tetra chlorinated congeners, particularly congeners 18 and 28. These 2 congeners consistently made up >20% of the ΣPCB load.

Soil concentrations peaked at between 140 (Luddington) and 560 μg ΣPCB/kg (Woburn) at the 5 sites, with the tri- and tetra- chlorinated congeners dominating the composition. These two homologue groups consistently account for >75% of ΣPCB in these samples. Peak PCB concentrations occurred between 1966-72.

The sharp increase in soil ΣPCB content between the 1940s and the early 1960s coincides with trends in the industrial manufacture of these chemicals, both in the UK and on a global scale. Nonetheless, it is interesting to note that environmental levels had probably started to increase during the 1940s, prior to UK production of PCBs in 1954. Between 1954 and 1977, when all UK sales were discontinued, a total of 66,748 t of PCBs were manufactured in the UK, with an estimated 40,000 t used within the UK. Global trends follow a similar pattern. Their widespread use in 'open' systems during this time is probably responsible for the observed substantial rise in soil levels.

An interesting feature of this time trend data is that ΣPCB concentrations on *Broadbalk and Hoosfield have declined substantially since their maximum* values in the late 1960s. Contemporary ΣPCB levels in Woburn soil samples are lower than those found in the 1942 sample. Levels at Luddington and Lee Valley exhibit a similar substantial decline. At each of the sites the concentrations declined at a greater rate during the early 1970s and then more slowly up to the present.

Changes in the levels of soil ΣPCB have mirrored changes in the ΣPCB content of herbage harvested at Rothamsted. Annual herbage PCB concentrations have declined substantially since the late 1960s, so that ΣPCB in samples from the late 1980s were just 2% of those between 1965 and 1969 (2). Interestingly, the timing of the peak and the pattern of decline in both soil and herbage at Rothamsted are similar. Vegetation harvested annually would be expected to reflect short term temporal variations in air quality. It is therefore interesting that the rate of decline in the soils is similar to that in the herbage, implying relatively short residence times of PCBs at the soil surface.

The declines in all of the long term experiments suggests that there has been a substantial reduction in the source of PCBs to the environment in rural southern England during the past 20 to 25 years, presumably because their use in 'open' systems has been limited. Whilst ΣPCB concentrations have declined in these soils since the late 1960s/early 1970s, concentrations of PAHs and PCDD/Fs at Rothamsted have increased (3, 4).

General comments

One fascinating feature of the time trend data is that ΣPCB concentrations at these sites have now apparently reverted to levels close to those in the mid 1940s, albeit with a somewhat different congener composition, with the heavier homologues constituting a greater proportion of the ΣPCB content. Clearly, manufactured 'Aroclor' inputs now exert a far less significant influence on ΣPCB levels at these sites than during the years of peak use. As an illustration of the scale of the reduction in levels of PCBs, if we assume that concentrations at the 5 study sites were/are representative of those in the UK generally (total surface area is 2.475×10^{11} m^2), that the soil density at the 5 sites averages 1300 kg/m^3 and that the soils were sampled to plough layer depth (23 cm), the ΣPCB burden of UK soils has declined from *ca.* 26 600 t (using mean of 360 μg ΣPCB/kg) to *ca.* 1 500 t (mean of 20 μg ΣPCB/kg) in the last two decades. In a recent survey

contemporary surface (0-5 cm) soils in NW England contained between 14 and 670 (median = 30) μg ΣPCB/kg, suggesting that the contemporary PCB concentrations in the long-term experiments studied are indeed broadly representative of soils nationally.

It is interesting to speculate on the ultimate fate of the PCBs lost from these soils. The most likely loss process is volatilisation. Volatilisation fluxes are temperature dependent and may result in PCBs from temperate latitudes, such as the UK, migrating by 'cold condensation' processes to the sub-Arctic and Arctic regions, where high concentrations have been observed far from local sources.

1. Alcock, R. E. *et al.*, Environ. Sci. Technol. (1993) in press.
2. Jones, K. C. *et al.*, Nature (1992) **356**: 137-140.
3. Jones, K. C. *et al.*, Environ. Sci. Technol. (1989) **23**: 95-101.
4. Kjeller, L.-O. *et al.*, Environ. Sci. Technol. (1991) **25**: 1619-1627.

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